METHYL TERT-BUTYL ETHER

Methyl tert-butyl ether is a federal hazardous air pollutant and was identified as a toxic air contaminant in April 1993 under AB 2728.

CAS Registry Number: 1634-04-4 $(CH_3)_3C(OCH_3)$

Molecular Formula: $C_5H_{12}O$

Methyl tert-butyl ether (MTBE) is a volatile, colorless, liquid at room temperature that is flammable when exposed to heat or flame. It is made from isobutene and methanol, which is derived primarily from natural gas. It is unstable in acid solution (Merck, 1989), and emits acrid smoke and irritating fumes when heated to decomposition (Sax, 1989). The smell is like that of ethers and turpentine and has a low odor threshold. Methyl tert-butyl ether is miscible with gasoline and is soluble in water, alcohol, and other ethers.

Physical Properties of Methyl tert-Butyl Ether

Synonyms: MTBE; tert-butyl methyl ether; 2-methoxy-2-methylpropane

Molecular Weight:	88.15
Boiling Point:	55.2 °C
Melting Point:	-109.0 °C
Flash Point:	-28.0 °C
Autoignition Temperature:	435 °C
Density/Specific Gravity:	0.7404 at 20/4 °C (water = 1)
Vapor Pressure:	245 mm Hg at 25 °C
Henry's Law Constant	5.87×10^{-4} atm-m^3/mole
Water Solubility:	4.8 g/100 g
Log Octanol/Water Partition Coefficient:	1.24
Conversion Factor:	1 ppm = 3.61 mg/m^3

(Howard, 1990; HSDB, 1993; Merck, 1989)

SOURCES AND EMISSIONS

A. Sources

MTBE is used as an octane booster in unleaded gasoline and as an oxygenate in gasoline. The Federal Clean Air Act Amendments of 1990 mandated that compounds that add oxygen (oxygenates) be added either in the winter or year round to gasoline in 39 specific parts of the country where concentrations of carbon monoxide in the winter or ozone in the summer exceed established federal air-quality standards. Gasoline sold in most of California was required to meet the federal requirement for oxygenates during the winters of 1992, 1993, and 1994. In Southern California it was required to be used year round beginning in January 1995.

In 1991 California adopted the cleaner-burning gasoline program, and to comply with federal standards, incorporated the federal requirements for oxygen. Neither the federal or state requirements for oxygen content require MTBE to be used as the oxygenate. That is the choice of the refiners.

California cleaner-burning gasoline was introduced in March 1996 and is sold statewide throughout the year. It can contain MTBE at 11 percent by volume to achieve a 2 percent oxygen content. Gasoline containing approximately 2 to 9 percent MTBE concentrations had been used sporadically in localized areas in California since the late 1970s as an octane booster but now is added to achieve the federal and state oxygenate requirements.

California produces about 5 percent of the total United States production of MTBE (California Environmental Protection Agency, 1997). The primary stationary sources that have reported emissions of MTBE in California are petroleum refining, pipeline services except natural gas, and the wholesale petroleum and petroleum products industries (ARB, 1997b). MTBE is added to gasoline at the refineries. The oxygenated gasoline is then dispersed through pipelines which transport most of California's fuel to end suppliers. Exposure to MTBE released during refueling at service stations is reduced by vapor recovery systems.

MTBE has been found in groundwater monitoring wells (not sources of drinking water) and in several drinking water sources (California Environmental Protection Agency, 1997). The primary source of MTBE in water is leaking underground storage tanks. All underground tanks must be upgraded (e.g., fiberglass and doublewalled) by 1998 to comply with federal requirements to prevent leaks. Water testing of California reservoirs has occasionally shown slight MTBE concentrations, probably due to boating and recreational watercraft activity. The United States Geological Survey found no MTBE in 100 agricultural and domestic wells in the San Joaquin Valley. Scientific projects to study MTBE in groundwater are planned as part of a comprehensive urban land use study in Sacramento and Los Angeles (Domagolski, 1997).

B. Emissions

The total emissions of MTBE from stationary sources in California have not all been reported but are estimated to be well over 28,000 pounds per year, based on early data entered under the Air Toxics "Hot Spots" Program (AB 2588) (ARB, 1997b). Automobiles using reformulated gasoline combust almost all MTBE; total organic exhaust emissions contain only approximately 2 to 3 percent MTBE (Allen 1997; Cleary 1997).

C. Natural Occurrence

Methyl tert-butyl ether is a man-made, synthetic compound which is not known to occur in the natural environment.

AMBIENT CONCENTRATIONS

There are ambient data from several states. Twenty four hour ambient air samples of MTBE were measured at an urban campus away from industrial sources in Milwaukee, Wisconsin. Eight samples were taken over a period of 6 weeks. The mean concentration was 0.72 microgram per cubic meter ($\mu g/m^3$) or 0.2 part per billion (ppb) with a range of 0.09 to 3.07 $\mu g/m^3$ (0.025 to 0.85 ppb) (Wisconsin DHSS, 1995a). The United States Environmental Protection Agency (U.S. EPA) has compiled data from several urban locations throughout the United States. Mean concentrations ranged from less than 0.7 $\mu g/m^3$ (0.2 ppb) in Boston, Massachusetts to 1.4 $\mu g/m^3$ (0.39 ppb) in Houston, Texas (U.S. EPA, 1993a) in 1990-91. A regional survey for a two-county area along the Houston Ship Channel near MTBE manufacturing facilities reported average ambient air concentration levels at less than 0.7 $\mu g/m^3$ (0.2 ppb) (U.S. DHHS, 1995).

Preliminary ambient air monitoring of MTBE in California has shown mean concentrations in the Los Angeles area of 14.4 $\mu g/m^3$ (4.0 ppb) with a range of 1.4 to 47.7 $\mu g/m^3$ (0.4 to 13.2 ppb); the central valley of 6.5 $\mu g/m^3$ (1.8 ppb) with a range of 4.3 to 11.2 $\mu g/m^3$ (1.2 to 3.1 ppb) (ARB, 1996e); and in the San Francisco Bay Area of 3.2 $\mu g/m^3$ (0.9 ppb) with a range of 1.8 to 27.1$\mu g/m^3$ (0.5 to 7.5 ppb) (BAAQMD, 1996).

Five documents on MTBE have received nationwide attention. In February 1996 the Health Effects Institute (HEI) released, “The Potential Health Effects of Oxygenates Added to Gasoline, A Special Report of the Institute’s Oxygenates Evaluation Committee” (HEI, 1996). In the same month the White House Office of Science and Technology Policy (OSTP) released a draft report entitled, “Interagency Assessment of Potential Health Risks Associated with Oxygenated Gasoline” (OSTP, 1996). These two documents were followed by the release in March 1996 of the draft document, “Interagency Oxygenated Fuels Assessment,” which addressed MTBE issues on health, air and water quality, fuel economy, and engine performance (OSTP, 1996). The latter document was peer reviewed by the National Academy of Sciences (NAS) under guidance from the National Research Council (NRC) who then published their findings and recommendations in the document, “Toxicological and Performance Aspects of Oxygenated Motor Vehicle Fuels” (NRC, 1996). The NRC findings were reviewed and the final report was released in June of 1997 (National Science and Technology Council, 1997).

INDOOR SOURCES AND CONCENTRATIONS

Data for air quality and microenvironments are too limited for a quantitative estimate of indoor air exposure. According to a New Jersey study done by the Environmental and

Occupational Health Sciences Institute, MTBE concentrations in automobiles during a commute were found to range from 18 to 275 $\mu g/m^3$ (5 to 76 ppb) (Lioy et al., 1993, 1994).

Air samples collected in Fairbanks, Alaska inside seven vehicles had concentrations less than 0.04 $\mu g/m^3$ (0.01 ppb) MTBE with the exception of the inside of one vehicle which was measured at 1.2 $\mu g/m^3$ (0.33 ppb) (Schweiss, 1993).

The ARB is funding research which will measure MTBE concentrations along with other volatile organic compounds inside vehicles (ARB, 1995h).

ATMOSPHERIC PERSISTENCE

MTBE exists in the atmosphere in the gas phase. The dominant atmospheric loss process for MTBE is by reaction with the hydroxyl (OH) radical. Based on this reaction, the atmospheric half-life and lifetime of MTBE are estimated to be approximately 3.5 days and 5 days, respectively. The products of the OH radical reaction include tert-butyl formate, formaldehyde, methyl acetate, and acetone (Atkinson, 1994).

AB 2588 RISK ASSESSMENT INFORMATION

No health values (cancer or non-cancer) for MTBE are listed in the California Air Pollution Control Officers Association Air Toxics “Hot Spots” Program Revised 1992 Risk Assessment Guidelines (CAPCOA, 1993).

HEALTH EFFECTS

Routes of human exposure to MTBE can include inhalation, ingestion, and dermal contact.

Non-Cancer: Acute exposure of humans to high concentrations of MTBE can result in nausea, vomiting, dizziness, and sleepiness. Direct exposure to the skin and eyes can cause drying and irritation.

An initial study of 1,500 individuals during spring 1995 in Madison, Wisconsin suggested that exposure to MTBE is not associated with widespread adverse acute health effects. The study did not rule out subtle effects or the possibility that some individuals may have a greater sensitivity to reformulated gasoline mixtures (Wisconsin DHSS, 1995a). A follow-up study on individuals who reported symptoms confirmed the conclusions of the initial study. Further investigation on potential effects of reformulated gasoline on the elderly and allergy sufferers was recommended (Wisconsin DHSS, 1995b).

Complaints of headaches, eye, nose, and throat irritation, dizziness, and nausea were recorded following the introduction in 1992 in Alaska of federal reformulated gasoline containing MTBE (15 percent by volume) for the reduction of carbon monoxide emissions. Follow up studies were unable to establish a correlation between these symptoms and exposure to MTBE (CDC, 1993a; 1993b). Studies of motorists and workers at gas stations and people whose occupations require extensive use of motor vehicles were conducted in Fairbanks, Alaska and Stamford, Connecticut during oxygenated fuels programs. Although a positive correlation was found between the concentration of MTBE in the air and blood concentrations, the blood concentration at which symptoms occur was not identified (U.S. DHHS, 1995).

In an experimental controlled chamber study, MTBE and its metabolite tert-butyl alcohol were readily measurable in the blood of humans exposed to 1.7 ppm MTBE for one hour, but no adverse symptoms were reported by exposed persons (Cain et al., 1993).

The U.S. EPA has established a Reference Concentration (RfC) for MTBE of 3.0 milligram per cubic meter (mg/m^3) based on increased liver and kidney weights, increased prostration in females, and swollen periocular tissues in male and female rats. This concentration is approximately 200 times greater than average ambient levels. The U.S. EPA estimates that inhalation of this concentration or less, over a lifetime, would not likely result in the occurrence of chronic non-cancer effects. The oral Reference Dose (RfD) is currently under review by the U.S. EPA (U.S. EPA, 1994a).

No information is available on adverse reproductive and developmental effects of MTBE in humans. Offspring of rats exposed by inhalation to high concentrations of MTBE (3,000 and 8,000 ppm) were reported to have reduced body weight, reduced body weight gain, and decreased pup viability. In mice, exposed through inhalation, decreased number of viable implantations, increased maternal toxicity, dead fetuses, late resorptions, and skeletal variations were reported at concentrations of 8,000 ppm (U.S. EPA, 1994a).

Cancer: No information is available on the carcinogenic effects of MTBE in humans. Inhalation studies in male and female mice reported an increased incidence of liver adenomas at concentrations of 8,000 ppm (Burleigh-Flayer et al., 1992), and carcinomas in male mice and possible renal tubular cell tumors in male rats at concentrations of 3,000 and 8,000 ppm (Chun et al., 1992). Studies are being analyzed to determine if the male rat renal tumor may be associated with α - 2μ - globulin nephropathy, which is thought to be unique to the male rat and not relevant to humans (Borghoff et al, 1996). Preliminary results from a study conducted in rats administered MTBE in olive oil by gavage indicate that MTBE induced leukemias and lymphomas in female rats at concentrations of 250 milligram per kilogram (mg/kg) body weight, and interstitial cell testicular tumors in males at concentrations of 1,000 mg/kg body weight (Belpoggi et al., 1995).

Animal evidence suggests that MTBE may be a weak carcinogen. The petrochemical industry and the U.S. EPA reviewed the results of a $3.5 million study on mice and rats exposed by inhalation to MTBE. At high concentrations, rats exhibited kidney lesions and tumors, and mice developed liver tumors. These data implied that MTBE may be a weak carcinogen. The U.S. EPA has not classified MTBE for human carcinogenicity but has indicated that MTBE could be considered as “having a human carcinogenic hazard potential”. They calculated two unit risk numbers: 7.5 x 10^{-8} $\mu g/m^3$ based on the mouse liver tumors and 1.7 x 10^{-7} $\mu g/m^3$ based on the rat kidney tumors (National Science and Technology Council, 1997).

At this time, the International Agency for Research on Cancer (IARC) has not classified MTBE for human carcinogenicity (IARC, 1987a). The State of California has not listed MTBE as a carcinogen under Proposition 65 (CCR, 1994).